CHAPTER II
THEORITICAL BACKGROUND AND LITERATURE REVIEW

2.1 Silk

Silk, is a natural protein fiber which has been used as a textile fiber for over 5,000 years (Mahmoodi *et al.*, 2010). Among several species of silkworms, there are two main types of silkworm which are mulberry silk (*Bombyx mori*), also called the "cultivated silk" and wild silk. Almost 80-85 % of the world production are obtained from the mullberry silk due to it is more fine, soft ,whiteness and luster than wild silk. However, some wild silk fibers are also used commercially because they have higher tensile strength and larger cocoon size. Thai silk is one of the mulberry silkworm (*Bombyx mori*) silks (Sonthisombat and Speakman, 2004).

The raw silk fiber is almost a pure protein fiber composed of two main components which are fibroin and sericin. Besides sericin and fibroin proteins, raw silk also contains other natural impurities, such as fat and waxes, carbohydrates, inorganic matter and pigment as shown in Table 2.1(Rajasekhar *et al.*, 2011).

Table 2.1 Composition of natural raw silk obtained from *Bombyx mori* (Rajasekhar *et al.*, 2011)

Components	**%**
Fibroin	70-80
Sericin	20-30
Wax matter	0.4-0.8
Carbohydrates	1.2-1.6
Inorganic matter	0.7
Pigment	0.2
Total	**100**

Silk fibers are extruded from two silkworm glands as a pair of primary filament. Fibroin, the real fibrous component, is extruded in pairs at a core of silk filaments, is glycoprotein composed of two equimolar protein subunits of 325 and 25 kDa, and is a main composition in the silk fiber and water insoluble protein. Fibroin is crystalline structure which has high proportion of glycine (43.7 %), alanine (28.8 %) and serin (11.9%). In the fiber, fibroin chains are aligned along the fiber axis, held together by a network of inter-chain hydrogen bonds forming the well known β sheet crystals (Figure 2.1)

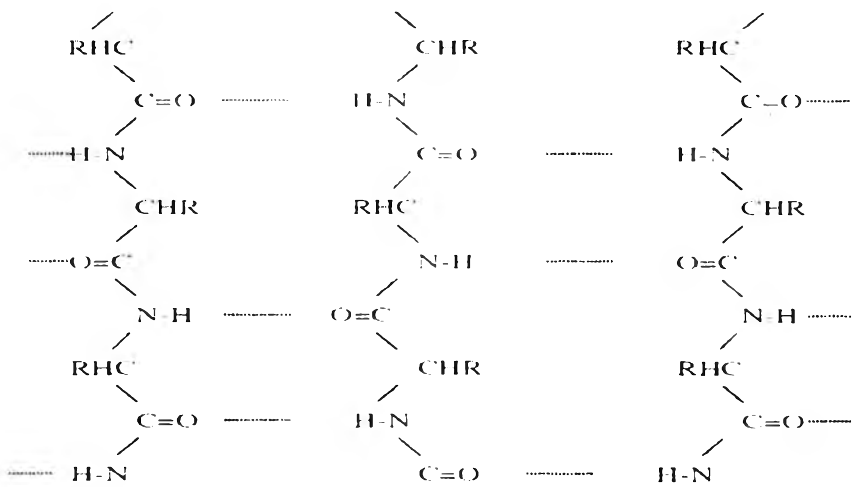


Figure 2.1 Crystalline structure of the peptide chains in silk fibroin form silkworm *Bombyx mori* (Mondal *et al.*, 2007).

Sericin, also known as silk gum gluing the fibroin filaments together, consists of glycine, serin, and aspartic acid totaling over 60 %. Sericin is a partially unfolded state composed of 35 % β sheet and 63 % random coil and it is dissolved in a hot water (Li et al., 2012). The sericin can be separated in 4 different forms as I, II, III and IV based on the order of ease of dissolution into hot water (Figure 2.2). Sericin IV is the innermost layer, which is close to fibroin and harder to dissolve in hot water (Roopesh Kumar *et al.*, 2012).

The processing of silk from cocoon to the finishing cloth consists of a series of steps which are reeling, waving, degumming, dyeing or printing and finishing.

However, degumming is the most important step to remove sericin and other unwanted impurities from raw silk.

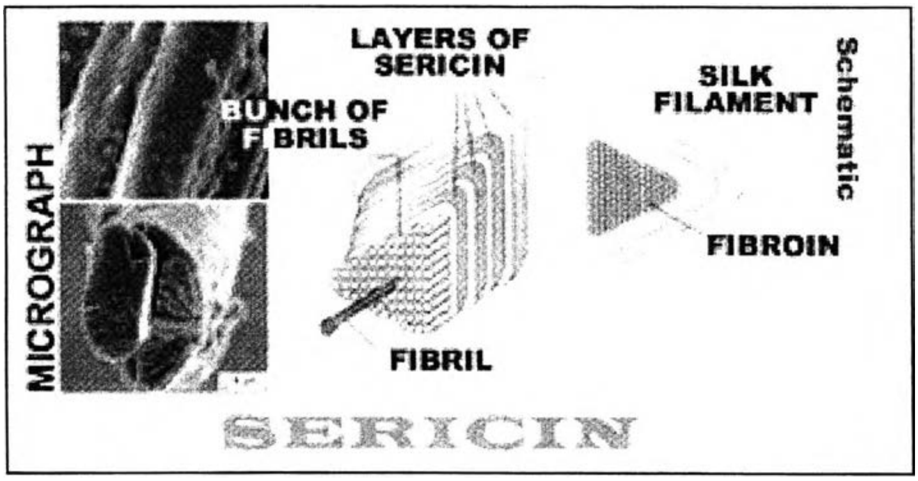


Figure 2.2 Composition of natural silk filament (http://www.fibre2fashion.com/industry-article/16/1510/a-value-added-finish-from-silk-degumming-waste-liquor1.asp).

2.2 Degumming Process

In order to meet the consumer's requests and get the good functional properties of silk, degumming process becomes one of the most important parts of the finishing process for silk yarn and silk fabric. The main purpose of this process is to remove sericin by breaking the peptide linkage of amino acid in the sericin structure into smaller molecules, which is soluble in water. The reason why we have to remove sericin because it gives dull appearance, which is a harsh and stiff feeling to the fiber and hides the whiteness, brightness and shininess of silk. Furthermore, it prevents its dye ability. During this process the sericin is removed from the fiber but the fibroin must not be damaged at the same time (Li et al., 2012). The pH range from 4 – 8 is safe for fibroin. On the other hand, the pH values between 1.5 and 2 and between 9.5 and 10.5 is suitable for removing sericin. After the degumming process, the two triangular fibroins will be separated into individual filaments which give different fiber geometry and properties from the raw silk, i.e. a finer fiber, a more whiteness fiber, soft fiber and a more lustrous fiber (Sonthisombat and Speakman, 2004).

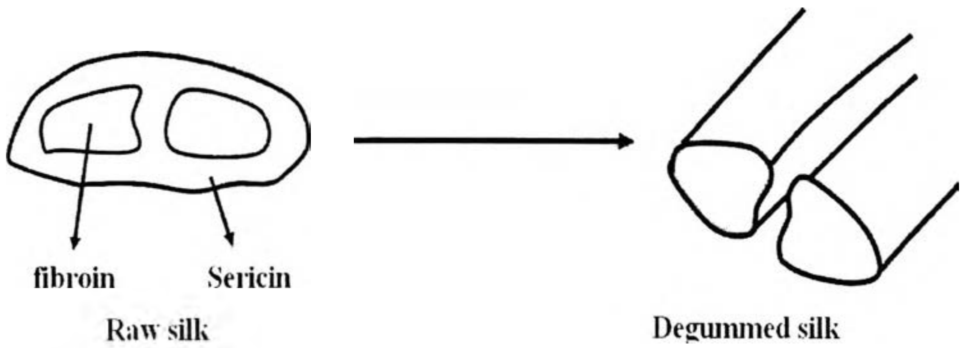


Figure 2.3 Cross section of raw silk and longitudinal section of degummed silk filaments (Sonthisombat and Speakman, 2004).

2.2.1 <u>Conventional Degumming Method</u>

A conventional degumming method is performed at high temperature (around 90 °C – 98 °C) and an alkaline pH (about 8-9) which can cause partial degradation of fibroin. A prominent soap for silk degumming is Marseilles soap (olive oil soap) (Sonthisombat and Speakman, 2004). Normally, sodium carbonate (also known as washing soda or soda ash) is used as an alkaline agent. Sasithorn and Luepong (2009) studied on silk degumming with dried latex of Carica papaya Linn. The purpose of the method was to compare with the conventional method. In the conventional degumming method, silk samples are treated with an alkaline bath which contains an aqueous solution of 10 g/L soap and 2 g/L sodium carbonate in a liquor ratio of 1:30 at 90-95 °C for 45 min. After that the degummed silk is washed with hot and cold distilled water and dried at room temperature. In 2009, Nakpathom *et al.* investigated the influence of papain enzymatic degumming of Thai Bombyx mori silk fibers on fiber damaged and residual sericin. The result of papain enzyme degumming was compared with a conventional alkali/soap method. In case of the conventional degumming, silk fibers is immersed in a boiled alkaline sotution containing 12 % of soap and 6 % of sodium carbonate for 60 minutes at a liquor ratio of 1:30 (g:mL). Degummed silk is then rinsed with cool and hot water and dried at 60 □ C.

2.2.2 Various Methods Silk Degumming

The hydrolysis reaction performed by soap/alkali in the conventional degumming method has a problem in term of surface area of silk. Furthermore, combination of soap and alkali is not an environmentally friendly method because it generates wastewater, and large water and energy consumption leading to environmental pollution (Li *et al.*, 2012). Nowadays, several methods have been developed and studied for silk degumming as follows:

2.2.2.1 Degumming by Enzymes

Proteolytic enzymes are used as eco-friendly degumming agents, which can operate under mind conditions and low temperature when compare with conventional method. However, this method has some disadvantages such as it was using a specific condition (pH and temperature) and expensive.

Freddi *et al.* (2003) studied the kinetics and mechanism of sericin removal with several proteases. Three different kinds of protease were used to treat raw silk fabric as degumming reagents. Those proteases were alkaline (3374-L, GC 897-H), neutral (3273-C), and acid (EC 3.4 23.18). Proteases were used at optimum condition of temperature and pH, while treatment time (5-240 min) and enzyme dosage (0.05-2 U/g fabric) were varied in order to study the kinetics of silk degumming. The conventional degumming (soap-alkali) gave degumming loss about 27 wt%. The result showed that alkali and neutral proteases were effectively degumming reagents, while acid protease was almost ineffective degummed silk fabric. The maximum amount of sericin removed in 1 h was 17.6 wt% for 3374-L (2 U/g fabric), 24 wt% for GC 897-H (2 U/g fabric) and 19 wt% for 3273-C (0.1 U/g fabric) respectively. The degumming kinetics were depended on enzyme dosage and treatment time and extended to a value of 25 wt% with 1U/g fabric of 3374-L. Sericin was removed completely from the warp yarns of the fabric, while on the highly twisted weft yarns sericin still exhibited (shown by morphology analysis), even though by using the standard conventional degumming method. A mixture of peptides varied from 5 to 20 kDa with a weight average molecular weight about 12 kDa was obtained with alkali and neutral proteases used in this study.

Anghileri *et al.* (2007) studied the effect of enzyme degumming on mechanical properties of silk yarn. Silk yarn was treated with two alkalines, a neutral and an acidic commercially proteases under optimum conditions of pH and temperature, while enzyme dosages were varied in 3 values (0.2, 1 and 5 U/g yarn). The results obtained from proposed method were compared with the standard method (soap) in term of physical and mechanical properties. The result can be concluded that the enzyme degumming is a promising and potentially more advantageous method than the conventional degumming. Both intrinsic properties (degree of polymerization) and mechanical properties (tensile parameters) showed similar or even better than the soap degumming of silk. Furthermore, the enzyme degumming can be operated in short time at lower temperature (65 °C) than the conventional silk degumming (98 °C).

Sasithorn and Luepong (2009) studied on the silk degumming with dried latex of Carica papaya Linn and its affective factors, such as temperature and time. The proposed method was compared with the conventional degumming. Tensile strength and staining test with direct dyes (C.I. Direct Red 80) were determined for the efficiency of degumming process. The result showed that the appropriate conditions were the amount of dry latex solution of 4% at 75 °C for 30 min in the neutral condition. and there was no damaged to strength and surface of fiber. The result of staining test with direct dyes was appeared pink which indicated that there was a small amount of sericin remaining on the silk fiber.

Nakpathom *et al.* (2009) investigated the influence of papain enzymatic degumming of Thai *Bombyx mori* silk fibers on fiber damaged and residual sericin. The papain enzyme obtained from local papyrus latex was used to degumming silk and compared with the conventional alkali/soap method. The result showed that the percents weight loss of both degumming processes were not significantly different (20-22%). Papain enzyme exhibited less tensile strength drop and obtained higher color depth after natural lac dying, especially when operated at room temperature.

2.2.2.2 Degumming by Acid

Several acids such as sulphuric, hydrochloric, tartaric and citric acids can be used to remove sericin from silk fiber. However, this method has not got much interest in the silk industry due to the degumming of silk from the alkaline solution safer for fibroin than in the acid solution. It has been found that strong mineral acids, such as sulphuric and hydrochloric acids cannot complete degumming of silk without harming to the fibroin (Sonthisombat and Speakman, 2004).

Khan *et al.* (2010) investigated the effect of citric acid treatment on physical properties and dyeability of silk fibers. The proposed method was compared with the traditional soap-alkali degumming method. The concentrations of citric acid were 15 % and 30 %, while the traditional method used marseilles soap and sodium carbonate as degumming agents. The result showed that the sericin removal from silk surface was almost completely after degumming with 30 % citric acid which resulted in a total weight loss of 25.4 % in the silk fibers. The morphology of silk degumming using citric acid obtained from SEM showed a smooth and clean surface. After the degummed silk with 15 % citric acid the tensile strength and elongation of degumming silk fiber were increased to 507 MPa and 20 %, respectively. On the other hand, the tensile strength obtained from the soap-alkali method was decreased about half of the control silk fiber (250MPa), which indicated the disordering of molecule orientation of silk fibers by the action of soap solution on the fibroin structure. However, The molecular conformation determined by FT-IR and the crystalline structure evaluated by X-ray diffraction curve stayed unchanged for both degumming with citric and soap. The dye ability was performed by dye uptake percentage, the silk degummed with soap was higher than citric acid degumming which implied the weakening molecular orientation of silk fiber, which was in agreement with the tensile result. It can be conclude that the degumming of silk fiber with citric acid is safe and promising.

2.2.2.3 Degumming by Ultrasonic

Mahmoodi *et al.* (2010) investigated the degumming of Persian silk using ultrasonic, ultrasonic-soap and ultrasonic-enzyme (alcalase, savinase and mixture of alcalase and savinase). They studied the effectiveness of parameters such as sonication time, soap, ultrasound-enzyme, enzyme, enzyme concentration degumming time and enzymes mixture on silk degumming. All of experiments under specified conditions showed that increase of the treatment time decreases the amount of sericin left over the surface of silk fabric. The ultrasound on silk degumming showed that the weight loss and strength loss of silk samples are negligible. The ultrasonic-soap showed that the ultrasound increases the rate of silk degumming by increasing the soap dispersion and diffusion capacities. For enzyme concentration, it can be concluded that increase of the enzyme concentration causes more weight loss and results in a decline in the filament strength.

Yuksek *et al.* (2012) studied on the effect of silk degumming with three different types of natural soap using an ultrasonic method on the properties of silk fiber. The Ultrasonic method (Branson B2200B E4) was carried out at 220 volt and 205 watt ultrasonic bath with 20 kHz. A treatment of 20 minutes was conducted at 60 □ C at a 1/30 flotte ratio to marsille and daphne and turpentine soap solutions were prepared at 0.7 % ratio with distillate water. The result was compared with the conventional degumming method. Degumming silk with turpentine soap showed positive result in terms of weight loss, whiteness and mechanical properties for both the conventional and the ultrasonic methods. Sonication is the reason of the accomplishment of ultrasonic energy method, which gives chemical substance, energy, water and time saving.

2.2.2.4 Degumming by Microwave

Haggag *et al.* (2007) studied the feasibility of using microwave-assisted treatment to enhance the extent of degumming of silk by savinase enzyme and other commercially degumming reagents, such as mineral acid, alkaline substances, domestic soap, and commercial protease. The result showed that the proteolytic enzyme savinase 16L type EX was effective in the degumming of silk either by the conventional method or in a combination with microwave. The microwave irradiation gave a level of degumming comparable with the traditional methods but with shorter treatment and lower concentrations. The result improved the level of degumming by using the microwave radiation and by the usual chemicals.

Mahmoodi *et al.* (2010) investigated the degumming of Persian silk using microwave irradiation as an environmentally friendly surface modification varying the parameters, such as microwave irradiation time, surfactant (sodium bicarbonate), soap (marseile), and degumming time on Persian silk degumming. The result showed that the amount of sericin remaining over the silk samples decreased. The result of this research supports the potential production of new environmental friendly process using microwave irradiation.

2.2.2.5 Degumming by plasma pretreatment

Long *et al.* (2008) developed a new method for raw silk fabric degumming with the application of low-pressure argon plasma in pretreatment combining a subsequent one-step mild wet-chemical process. The plasma parameters were investigated, such as argon press, discharge power and exposure time. The result showed that an optimized plasma pretreatment condition for raw silk fabric degumming was at 80 Pa of argon gas and 60 W glow discharge power for 5-10 min. The degumming efficiency and properties of silk fabric that performed by the proposed method achieved comparable with the conventional degumming process. Moreover, it was more environmentally friendly method.

There are several methods used to evaluating the efficiency of silk degumming process, such as the gravimetric method, staining methods with some dyes that separate between fibroin and sericin, determination of viscosity of the degumming solution and SEM (Sonthisombat and Speakman, 2004).

2.3 Basic Principles of Plasma

Plasma can be defined as a partially ionized gas containing highly excited ionic, radical species, atomic, molecular, photons and electrons, known as the fourth state of matter (Figure 2.4), which is the highest energy. The term of "ionized" is an atom or molecule which at least one electron has been adding or removing and then, they may generate new ion and neutral species. The present of free charges make the plasma electrically conductive so that they can couple strongly to electromagnetic fields. According to plasma history, the plasma was first identified by Sir William Crookes in 1879 and the term "plasma" was called by Irving Langmuir in1928 (http://www.en.wikipedia.org).

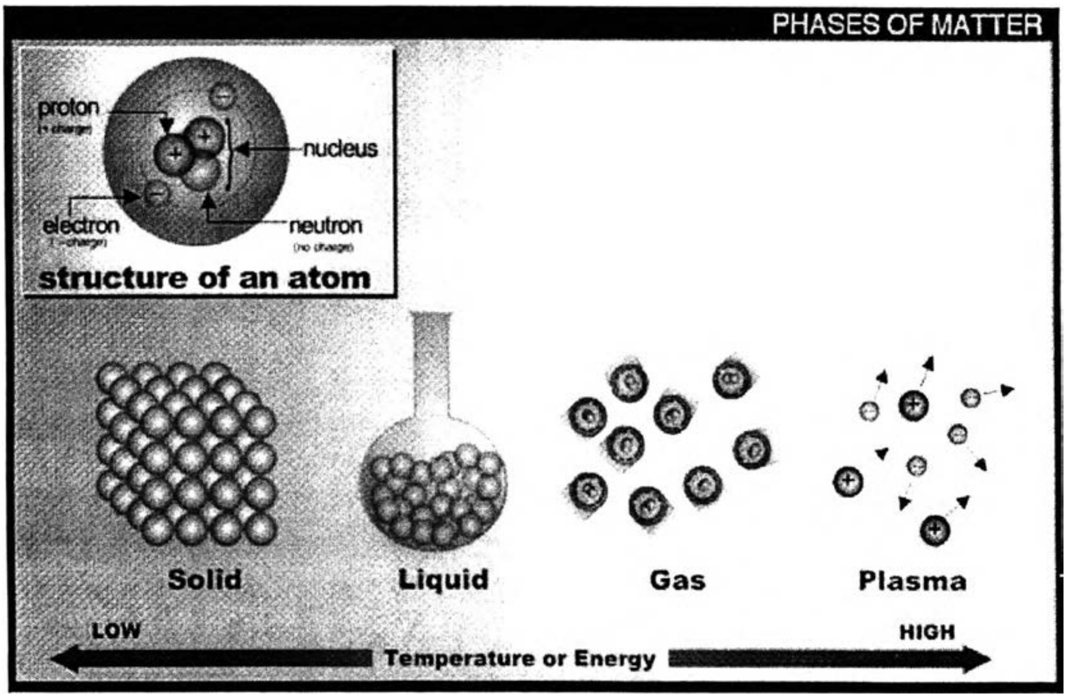


Figure 2.4 Phase of matter consists of solid. liquid, gas and the fourth state named "plasma"
(http://www.nasa.gov/mission_pages/themis/auroras/sun_earth_connect.html.)

It consists of negative charges (either electron or anions) and positive charges (mostly cations) as well as neutral (atoms or molecule), which may be the mixture between free radical species and stable neutral gases. Plasma possesses have two significant properties quasi-neutral property and interaction with electromagnetic fields (Eliasson and Kogelschatz, 1991).

Quasi-neutral property is a state that plasmas contain equal numbers of positively charged ions and negative charged electron. In fact, plasma cannot contain exactly equal numbers of positive charged ions and negative charged electron, but the number of charges is huge and the difference is relative small, so the term "quasi-neutrality" is an for approximation.

Interaction of plasma with electromagnetic fields can happen upon applying of an electromagnetic field due to the charged particles in the plasma.

Generally, plasma can occur in all states (Nasser, 1971). Plasma in solid is called solid-state plasma, while plasma generated in the liquid and gaseous states does not have any specific names. Only gaseous plasma is shortly called as "plasma". There are many differences between plasmas and gases including pressure, distributions of charged-particle density in the entire plasma volume, and temperature.There are three types of plasma reactor depending on a power supply which can generate plasma. low-frequency (LF, 50-450 MHz), radio-frequency (RF, 13.56 or 27.12 MHz), and microwave (MW, 915 MHz or 2.45 MHz) (Aasim, 2007).

Plasma can be classified into two types, thermal and non-thermal plasma of thermal. In thermal plasma (hot plasma), the temperatures of gas and electrons are approximately equal to close to the thermodynamic equilibrium temperature. Plasma particles have a uniform temperature and are in the very high temperature discharge region. Thermal equilibrium among all plasma species is the characteristic of thermal plasma. An essential condition for the formation of thermal plasma is sufficiently high working pressure and high gas density, so that the frequency of collisions between electron, ion, and neutral species composing the plasma is possible for an efficient energy exchange. Thus, it will leads to rapid redistribution of energy and to reach equilibrium (Shishoo, 2007).An example of this plasma is arc discharge and plasma torches. One application of thermal plasma technology is waste management solutions. It offers a wide range of advantages over the other for waste management solutions. Owing to high temperatures, it can change the state of wastes to destroy hazards. This technique is also highly flexible and easy to control and, a low impact on environment. Huang and Tang (2007) reviewed organic waste treatment using thermal plasma pyrolysis technology and Gomez *et al.* (2009) reviewed the current state of waste treatment using plasma technology. They concluded that the thermal plasma technology has been continued advances towards the further development in environmental field.

Non-thermal plasma or cold plasma is not in thermodynamic equilibrium due to low density of the plasma gas that collisions with the other species are relatively rare, which is characterized by a low gas temperature and high electron temperature. The non-thermal plasma is performed at room temperature or a slightly higher than room temperature. The bulk temperature of the ionized gas is about room temperature. According to the low operating temperatures, cold plasma is particularly suited to apply to textile processing without problems because most of textile materials are heat sensitive. (Shishoo, 2007, Morent *et al.*, 2008). The non-thermal plasma can be classified into several types depending upon their generation mechanism, their pressure range and the electrode geometry. Examples of this plasma are corona discharge, glow discharge and dielectric barrier discharge.

2.3.1 Types of Non-Thermal Plasmas

There are two types of non-thermal plasma which can be used for treatment of textiles, vacuum pressure and atmospheric pressure. In the fact, plasma cannot be performed in a complete vacuum, so the name of vacuum pressure may lead to misunderstanding. It is only referred to a low pressure condition of system (Aasim, 2007. Shahidi *et al.*, 2013). According to Aasim (2007), the vacuum pressure plasmas are classified into subcategories of low and medium pressures. (Table 2.2) However, due to small pressure difference between the sub classes of vacuum plasma, so non-thermal plasma will be classified in to two main types, vacuum pressure plasmas and atmospheric pressure plasmas.

Table 2.2 Operating pressures of vacuum and atmosperic plasmas(Aasim, 2007)

Pressure		Pressure Units			
		kPa	Torr (mmHg)	Atmosphere (atm)	Bar
Vacuum	Low	0-0.29	0-2.175	0-0.003	0-0.0029
	Medium	0.3-7	2.25-52.5	0.003-0.069	0.003-0.07
Atmospheric		101.3	760	1	1.103

Vacuum pressure plasma

Vacuum pressure plasmas are substantiated methods for surface modification. The plasma treatment under vacuum pressure are the most common plasma teratment for textiles.Normally, the working pressure is kept as low as 0.1 mbar for operating with the radio frequency range (typical 40 kHz or 13.56 MHz) or, a working pressure between 0.5 and 1 mbar for microwave.However, a base pressure has to be reached in the low level of 0.01 mbar in order to get effective plasma treatment in sufficienly pure process gas conditions. This base pressure can be performed with two-stage roughing vacuum pumps(rotary vane type) or with a dry pump or with a combination of one of those pumps with roots blower (Shishoo, 2007). The main drawback of this type of plasma is the operating pressure range allows only batch process. Also, the cost of maintenance is expensive. However, it has an advantages in term of application such as etching and coating which can be performed better under the vacuum pressure plasmas (Aasim. 2007). Other advantages of plasma , like uniform glow, low breakdown voltages, high concentration of reactive species (Kale and Desai. 2011).

Atmospheric pressure plasma

Atmospheric plasma is operated at atmospheric pressure, so it can be used for a continuous treatment. This type of plasma is evolved to fulfill the need of textile industry, but some applications are limited because only effects loosely on fiber surface and lacks of ability to penetrate into a fabric sttructure. Furthermore, the atmospheric plasma liberae of ozone gas and nitrogen oxides at workplace which is not safe for human (Aasim, 2007). There are different types of non-thermal plasma, *corona discharge, dielectric barrier discharge, and glow discharge.*

Corona discharge is the oldest type of plasma treatment for textile. It is characterized by bright filaments extending from a sharp, high-voltage electrode towards the substrate (Figure 2.5). The corona discharge consists of rapid, non-uniform, non arcing discharge (Shishoo, 2007, Deshmukh and Bhat, 2011). The advantage of this type of non-thermal plasma is that it is easily formed at atmospheric pressure by applying dielectric current, low frequency or pulsed high voltage over two electrodes of very different size (Aasim, 2007, Shahidi *et al.*, 2013). The corona plasma is too weak and too inhomogeneous to treat textile and cannot be used for treating thicker fabric. In fact, the corona systems are effectively only in loose fibers and cannot penetrate deeply into yarn or woven fabric. Plasma density drops dramatically with increasing a distance from the electrode.

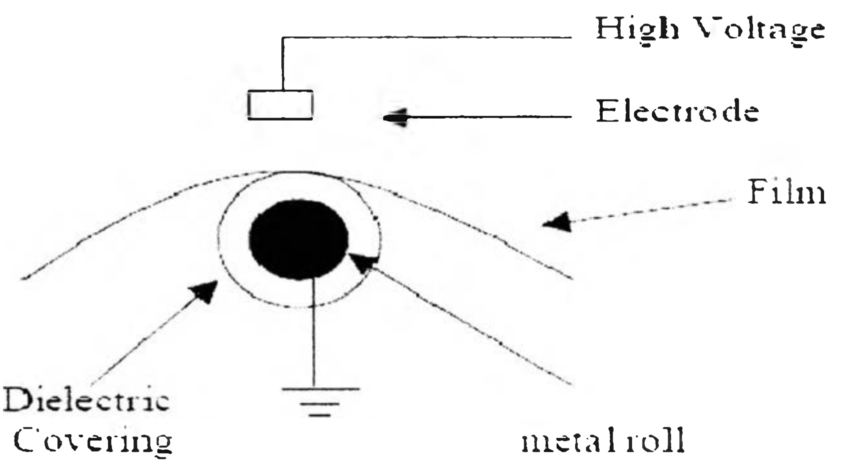


Figure 2.5 Schematic diagram of corona discharge (Ubaid and Danish, 2010)

The dielectric barrier discharge (DBD) is a wide class of plasma source which has an insulating (dielectric) cover over one or two of electrode and its operated at high voltage power ranging from low frequency alternating current (AC) to 100 kHz, which results in the non-thermal plasma and a multitude of random, numerous arcs between the electrodes. It is an atmospheric pressure plasma source. The objective of the dielectric layer is to confine rapidly the arcs forming in the region between electrodes. The dielectric discharge consists of rapid micro-discharges. However, these micro-discharges are non-uniform and have potential to cause uneven treatment occurring (Shishoo, 2007). Figure 2.6 shows a schematic of the dielectric barrier discharge with a symmetrical electrode arrangement.

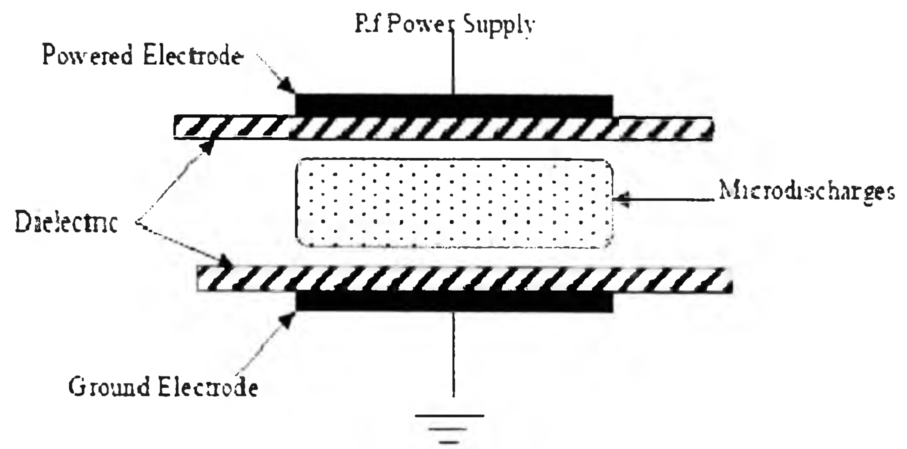


Figure 2.6 Schematic of dielectric barrier discharges (Ubaid and Danish, 2010)

Glow plasma is obtained at low pressures, normally less than 10 mbar. The plasma is generated by antennas, fed with electromagnetic fields at frequencies of 40 kHz or 13.56 or microwaves (2.45 GHz) , usually generated between the flat electrodes. The glow can be produced by applying a potential difference between two electrodes in a gas. Since the pressure is typically lower than 10 mbar, the reduced field or the electric field divided by the neutral gas density can therefore be quite high, which is a characteristic of non-thermal plasma. The glow discharges is quite popular due to the comparatively low voltage and current needed to operate and become an important laboratory tool for plasma chemical investigations. There are some practical applications of glow discharge in light industry such as neon tubes (for outdoor advertising) and fluorescent tubes. The glow discharge is characterized as a uniform, homogenous and stable discharge. Helium and argon (and some in nitrogen) are usually used as working gas (Shishoo, 2007).

The electric field is generated by a direct current. Direct current (DC) glow discharge is a self-sustained continuous DC discharge having a cold cathode, which emits electrons as a result of secondary emission mostly induced by positive ions. Important outstanding features of a glow discharge are large positive space charge and strong electric field. The thickness of the cathode surface is inversely proportional to gas density and pressure. The distance between electrodes is sufficiently large, Quasi-neutral plasma with a low electric field, the so-called positive column. is formed between the cathode and anode layers, as shown in Figure 2.7.

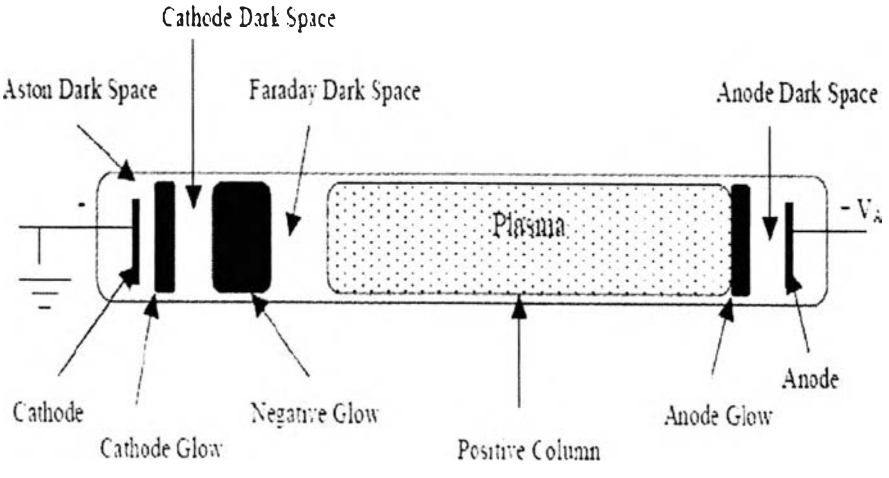


Figure 2.7 General structure of a glow discharge device (Kan and Yuen, 2006).

The DC glow discharge is normally used as a sputtering source for metallic materials. However it is limited in use for many industrial applications due to it has a narrow range of operating pressure. Another limitation is the inability to use for treatment insulating material over the electrodes. For these limitations, radio frequency discharge is more popular for practical plasma process (Kan and Yuen, 2006).

Radio frequency (RF) glow discharge is the common alternating current (AC) discharge which was used in plasma technology. When the applied frequency is high enough (13.56 MHz is the standard industrial frequency). RF discharge can be divided into inductive. capacitive and microwave discharges. in which they are differed by the way of RF is generated in the discharge space. There are two types of inductively driven sources. cylindrical and planar geometer as shown in Figure 2.8. The inductive discharge (inductively coupled RF discharge) has been studied in both atmospheric and vacuum regimes. However. the vacuum regime is more popular than atmospheric pressure because the high ion density of the vacuum pressure (Kan and Yuen. 2006).

The capacitive discharge (capacitively coupled RF discharge) plasma is the most commonly used for materials processing. The capacitive plasma is essentially consists of two parallel electrodes separated by small distance, placed in a vessel filled with working gas at constant pressure and RF voltage is applied across the electrodes. The geometry of electrode can be symmetric or asymmetric in diameter. Figures2.9 shows a schematic diagram of parallel plate capacitive plasma reactor representing a conventional device (Kan and Yuen, 2006).

The microwave discharge known as wave-heated discharge uses higher frequency (2.45 GHz) than the inductive and capacitive and capacitive discharge which are widely used because the microwave discharge requires large applied magnetic field for the frequency of 2.45 GHz (Kan and Yuen, 2006).

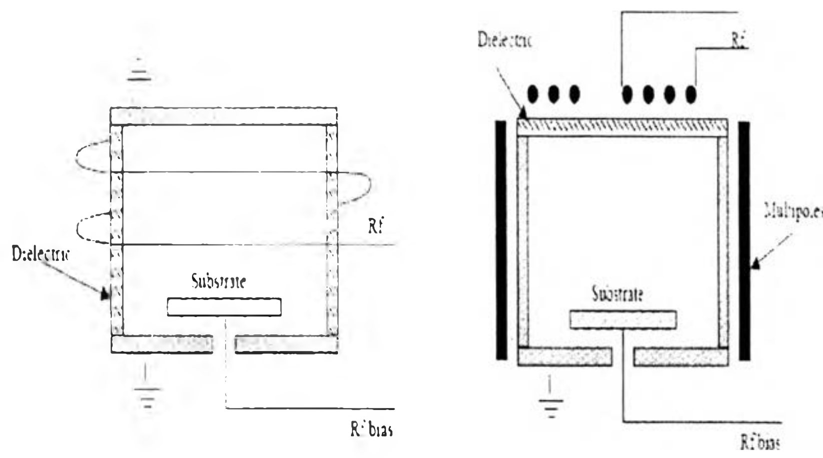
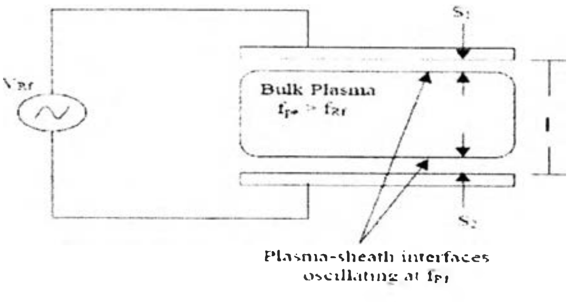


Figure 2.8 Schematic diagram of inductively driven sources in (left) cylindrical and (right) planar configuration (Kan and Yuen, 2006).



Figures 2.9 Schematic diagram of parallel plate capacitive plasma reactor (Kan and Yuen, 2006).

2.4 Plasma–substrate Interaction

The reactive species, such as positive and negative ions, atoms, neutrals and free radical are generated by ionization, fragmentation and excitation. All of reactive species lead to chemical and physical interactions between plasma and surface substrate. To study the potential applications of the plasma in the textile, it is important to understand the interaction or phenomena which may occur on the textile substrate. Several phenomena can occur depending on the nature of the gas and operating conditions such as, power, pressure, frequency, and exposure time. Figure 2.10 showed the possible mechanisms for plasma and substrate interaction which are etching, chain-scission, radical formation, grafting , cross-linking and polymerization (Kale and Desai, 2011).

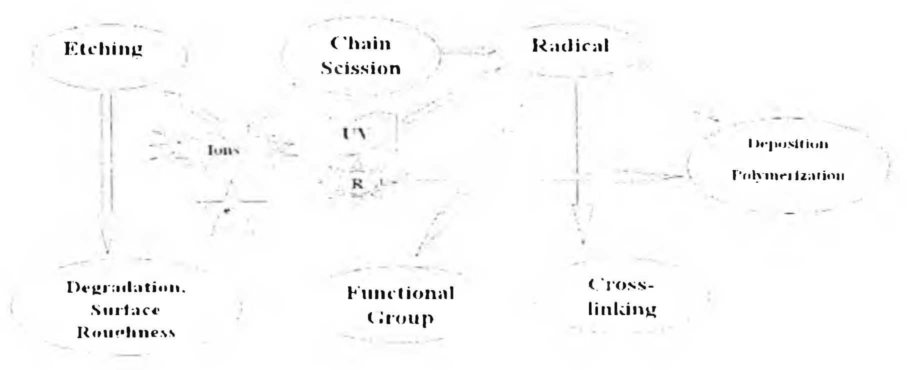


Figure 2.10 Mechanisms of plasma and substrate interaction (Kan and Yuen, 2006).

Kale and Desai (2011) reviewed the atmospheric pressure plasma treatment of textiles using non-polymerizing gases. Plasma interaction with the surface can be classified into two types, i.e. non-polymerizing gases and polymerizing gases as shown in Figure 2.11. The first type of plasma etches, cleans, or activates a surface by chain scission of the surface substrate, which results in the breakage of the substrate polymer molecule into smaller parts, causing weight loss and a reduction in molecular weight. Non-polymerizing gases, such as helium, argon, oxygen, air and nitrogen can be used to obtain this type of phenomena. The second type, polymerizing gas plasma refers to plasma inducing polymerization or grafting which can be carried out by using polymerizing gases and precursors like fluorocarbons, hydrocarbons and silicone containing monomers.

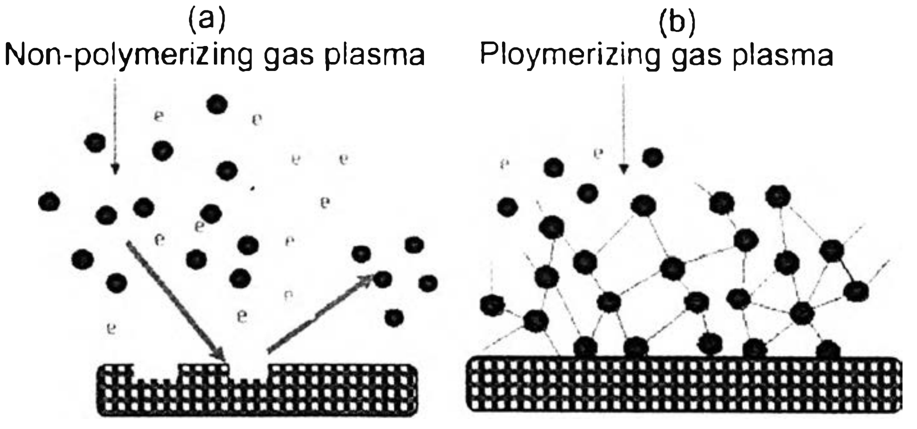


Figure 2.11(a) Non-polymerizing gas plasma [Etching/cleaning/ablation] (b)Polymerizing gas plasma [grafting/polymerization] (Kale and Desai, 2011).

2.5 Etching

Plasma etching is the key process for removal of surface material from a substrate, also can remove impurities from the substrate. The bombardment of the substrate with the plasma species causes the breakdown of covalent bonds. As a consequence, low molecular weight species will be removed (Shishoo, 2007). Etching can be occurred by physical sputtering or chemical reaction and ion-assisted mechanisms (Kan and Yuen, 2006). The simple mechanism for etching can be explained that the surface of substrate under plasma treatment is etched or scraped out by reactive process gas, then those materials are vaporized and drained off to be removed from the surface (Aasim, 2007). The surface etching extend ability is dependent of plasma-surface interactions, which are varied with the plasma parameters, such as gas, pressure, exposure time and power.

A type of working gas and its flow rate also influence on the etching phenomena. By adjusting one of two parameters degree of etching will change. Especially, the gas type will induce a higher or lower degree of etching. Generally, inert gases (argon and helium), nitrogen or oxygen is used as an etching gas (Shishoo, 2007). Compounds that contain oxygen are commonly used as etching gases because oxygen is an oxidant/etchant gas, and surface etching is a usual occurrence when material is treated with oxygen plasma (Canup, 2000). Helium is much preferred as carrier gas over the others due to its high energy meta-stable state and excellent heat conductivity, but its cost is very expensive (Kale and Desai, 2011). Long *et al.* (2008) developed a new method for raw silk fabric degumming with the application of low-pressure argon plasma. The etching was observed with pits or grooves on the fabric surface. Junkar *et al.* (2009) studies treated PET foil by low-pressure plasma RF nitrogen and oxygen plasma. The result was revealed by AFM showing that oxygen plasma produces higher surface roughness compared to nitrogen plasma treatment because of etching.Vesel *et al.* (2009) studied the surface modification of a viscose textile which was treated by oxygen, nitrogen and hydrogen plasma. The results obtained from SEM showed that nitrogen plasma did not cause any significant changes in the surface of the textile fiber, but after the treatment in hydrogen or oxygen plasma, the surface became rougher. In addition the effect of gas flow rate must be considered. Generally, the rate of etching will increase rapidly with increasing flow rate to a maximum value. However, the flow rate cannot increase to the maximum value because raising of pumping speed may bring active species to be pumped away before having the chance to react which will decrease the etch rate for the high flow. Thus, the gas flow rate has to be optimized (Chapman, 1980).

Working pressure is found to be the most important parameters in the etching mechanism because it is directly affect to the major phenomena which control the etching process. The phenomena are the sheath potential and energy of ions bombarding the surface, the electron energy, the ion-to-neutral abundance ratio and fluxes to these species to the surface, the relative rates of mass transport process and it also determines the mean free path of the particles in the gas phase and their penetratation to the substrate structure. At the pressure below 0.1 Torr (vacuum plasma system), the sheath potential dramatically increase, so the pressure is inversely proportional to the mean-free path, which gives a higher energy of ion flux. As a consequence, the ion bombardment promotes etching by physical sputtering (Manos and Flamm, 1989).

The influence of operating power is straightforward, i.e. increase of power increases both of density and the energy of the free electrons. In general, it is believed that higher operating power will be capable of etching substrate at a faster rate. However, if the operating pressure is too high melting and merging of substrate may occur (Tsoi *et al.*, 2010).

For exposure time, Gupta *et al.* (2000) studied the surface modification of polyester films by RF plasma. The result from atomic force microscope (AFM) analysis showed progressively rougher surfaces with increasing exposure time in argon plasma. Kan (2007) studied a time dependence of treated wool by low temperature plasma. The results showed that the scale structure on the wool surface diminished gradually with the increasing treatment time.

2.6 Surface Morphology and Surface Chemical Analysis

Due to the etching phenomena on polymeric surface, morphology and topographical changes will occur. These changes can be evaluated through scanning electron microscope (SEM) and atomic force microscopy (AFM). Furthermore, after etching process chemical composition of surface may change. Fourier transform infrared (FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS) are wildly used for surface chemical analysis where chemical characterization near the surface region up to 1-2 nm can be determined (Kale and Desai, 2011).

2.7 Application of Non-thermal Plasma on Silk

Since the gaseous plasma is an effective source of active species and system overall being at room temperature, it allows the surface treatment of fibers and textiles without effecting on their bulk properties. Accordingly, it leads to numbers of research on plasma surface treatment on textile.

Chaivan *et al.* (2005) investigated the plasma parameters that are suitable for textile treatment and to increase the hydrophobic property of Thai silk. The SF_6 was used as working gas to improve hydrophobic property of silk. The plasma was generated by an inductively coupled 13.56 MHz discharge. The plasma was confined by arrays of permanent magnet buttons. The working pressure was at 1, 3, 5 and 7 mTorr while the RF working power was varies from 25 to 75 W. The SF_6 plasma parameters were measured at the center of the chamber of reactor. An electron temperature was about 3-5 eV and an ion density was $1.0\text{-}3.5 \times 10^{10}$ cm^{-3}.The result of an optical emission spectroscopy showed the mixture of fluorine ion inside the plasma. The hydrophobicity improvement of silk was achieved. The treated samples reached the limit absorption time at180 min and contact angle was increased to 130-140 °. The optimum conditions of the system were an RF working power around 50 W and a working pressure of 3-5 mTorr. The plasma became unstable at an RF working power over 50 W and a working pressure over 5 mTorr.

Li and Jinjin (2007) improved the hydrophobic properties of silk and cotton by a hexafluoropropene (C_3F_6) plasma treatment. The plasma surface treatment of silk and cotton fabric were carried out in C_3F_6 gas under different conditions. A GPT-3 glow discharge was used in this work. The results showed that C_3F_6 plasma treatment improved the hydrophobicity of the silk and cotton remarkably. Both silk and cotton after treated with plasma only 1 min. contact angles reached 120° or higher while wet-out time can be as high as 50 min. The result obtained from X-ray photoelectron spectroscopy (XPS) revealed that about 50 % or more of fluorine atoms were incorporated in the surface of two fibers. Tensile strength increased after plasma treatment and the treated fibers still have high vapor permeability as untreated fibers.

Hodak *et al.* (2008) studied the surface modification of Thai silk plasma. The SF_6 operating pressure, the RF power and exposure time were varied to find the optimum conditions for improvement of the hydrophobicity of Thai silk. The plasma was generated by the radio-frequency inductively coupled 13.56 MHz discharge in a cylindrical stainless steel. The working pressure was at 0.005, 0.05, 0.5 and 1 Torr while the RF working power was adjusted to 25, 50 and 75 W. The exposure time was at 1 or 5 min. The result showed that the water contact angle of the untreated silk fabrics increased from 0° up to 145° after SF_6 plasma treatment. For the pressures lower than 0.05 Torr, the water absorption time was found to depend on the treatment time and RF working pressure. At higher pressures, all sample treatment achieved absorption times in excess of 200 min. After plasma treatment, the surface roughness of fibers increased from 10 to 30 mm. The results indicated that the hydrophobicity improvement of Thai silk fabrics can be achieved by treatment with SF_6 plasma. The optimum operating conditions for obtaining high water absorption times are pressure higher than 0.05 Torr and RF power of 50 W at exposure time range from 1-5 min.

Park *et al.* (2008) investigated whether microwave-induced argon plasma at atmospheric pressure can sterilize the microorganisms in silk fabrics or not. Also, the influence of the plasma treatment was determined on the physical properties of the fabrics. The results showed that the silk fabrics could be completely sterilized by the microwave-induced argon plasma. Furthermore, the plasma treatment did not effect on the ultimate tensile strength and surface morphology of the fabrics but it decreased the lightness of the fabrics.

Suanpoot *et al.* (2008) studied the plasma process in order to optimize the plasma parameters for the improvement of the wettability of silk. Thai silk was treated under different conditions by a discharge of sulfur hexafluoride (SF_6) gas in a low pressure radio frequency reactor, knows as inductively coupled plasma (ICP). A pressure was ranged of 10-300 mTorr while the RF power input was in a range of 20-100 W. The results showed the efficiency of SF_6 plasma on improving of hydrophobic property of the Thai silk.

Chaiwong *et al.* (2010) studied the application of atmospheric pressure plasma jet to graft phosphorus-based flame retardant agent onto silk. Argon gas was used as a working gas with an inner electrode was connected to a 50 kHz, 0-10 kV voltage source whereas an outer electrode was grounded. The result was evaluated by 45 ° flammability tests and showed that the treated fabric had a higher level of flame retardancy. It was found that the argon plasma gave durable flame retardancy to the treated fabric since the flame retardant character remained after the washing process. The result was obtained from scanning electron microscope and showed that the yarn of treated silk was uniformly covered with the PBS particles. The presence of phosphorus up to 11wt % was found on the argon treated silk. Covalent bonds between phosphorous and molecular chains of silk were confirmed by molecular dynamic (MD) simulations and FT-IR.

Gogoi *et al.* (2011) studied the surface modification of muga silk fiber by improving their tensile strength and hydrophobicity using argon plasma treatment. Furthermore, the plasma discharge characteristics were investigated at different plasma condition. The capacitively coupled radio frequency plasma was used to generate plasma with an argon gas at various RF power (10-30 W) and treatment times (5-20 min.). The argon discharges were measuring using self-compensated planar Langmuir probe and emissive probe. The results showed that both the electron temperature and plasma density (electron and ion density) was increased with increasing RF working power. A thermal behavior of the treated fiber was not changed by the variation in treatment time and RF power. The result was obtained by XPS showed significant changed in a chemical structure of the fiber at a higher RF power (30 W). The chemical compositions of the treated fibers were observed to be affected by increasing RF power rather than treatment time. The result showed that the tensile strength and hydrophobicity of treated fibers were found to be dependent on the variation in atomic concentration and functional composition at the surface. At RF operating power at 10 W and treatment range of 5-10 min, the properties of treated fibers were similar to that of the virgin one. At RF power of 20 W and lower treatment time (5-10 min), the plasma treatment fibers reveal enhanced tensile strength and hydrophobicity. On the other hand, at higher RF working power (30 W) and the increase the treatment time debased the properties of the fiber due to the surface degradation by sufficiently high energy ion bombardment.

Kamlangkla *et al.* (2011) studied multifunctional silk fabrics by an argon plasma induced graft polymerization (PIGP) process. The low pressure microwave plasma with a tunable power ranging from 0 to 600 W was used to generate plasma. Diethylacryloy-loxyethyl-phosphate (DEAEP) and -phosphoramidate monomer was used as flame retardants. After applying the PIGP process of two phosphorous, the fabrics with a flame retardant were exposed to SF_6 plasma to improve their hydrophobicity. The result of flame retardant showed that the phosphoramidate monomer decreases more the flammability of the silk fabrics than the phosphate. In the second step. After 5 min of SF_6 treatment, the fabrics which were originally absorbent became water repellent and showed an apparent contact angle of 134°. However, this property remains only several weeks of air exposure.

According to the theoretical background and literature review, a new degumming method by plasma treatment should be studied because the plasma process is one of environmental friendly process which can reduce huge amount of wastewater and energy consumption. In addition, there is no specific study has been reported for only the effect of plasma treatment to the degumming of silk. In this study, Low pressure plasma with glow discharge type was used to study the effect of plasma parameters on the degumming process of Thai silk. The plasma treatment was operated at discharge power of 60, 250, 1000 and 2000 W, exposure time was varied at 5, 10 and 15 min with oxygen flow rate at 250, 500 and 1000 cc/min and temperature chamber was varied at 25, 50 and 75°C. Oxygen gas was used as etching gas.